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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Coloured Resins

We, ALLIED CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the colouring of synthetic resins, especially synthetic resins which in the normal form (that is, in the uncoloured form as usually obtained in commerce or in commercial manufacture) are clear, substantially water-white, glass-like thermoplastic solids.

The synthetic resins form a large and commercially valuable class of synthetic materials, which include both thermoplastic polymeric materials, e.g. polystyrene, polymethylmethacrylate, polyvinyl chloride and vinylidene chloride polymers and copolymers, polyethylene, polypropylene, fluorohydrocarbon polymers, cellulosic esters and ethers, and copolymers containing at least one of said materials and thermosetting resins such as silicone, urea-formaldehyde, melamine-formaldehyde, melamine-urea, and phenol-formaldehyde resins. Plastic substances of this class possess the characteristic property of flowing at least under the initial application of heat and pressure and consequently have been employed extensively in moulding processes to produce useful articles. Many of these have been coloured in order too increase their utility and attractiveness.

The range of colorants suitable for such resins is very limited, however, particularly for the production of clear, glass-like, coloured products. Because of the tendency to use higher processing temperatures and pressures, organic colorants formerly suitable, i.e. capable

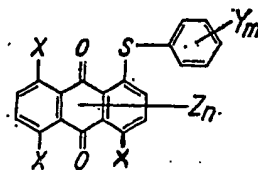
of withstanding the processing conditions without alteration of shade or loss of fastness or other desirable properties, have proved to be unsatisfactory to meet current demands.

In general, the conditions currently employed in processing even thermoplastic resins are too drastic for most organic pigments; and hence inorganic substances, such as carbon black, iron oxides and cadmium selenides, have been utilized to impart colour to thermoplastic resins. However, inorganic pigments give colorations lacking in the brightness and/or clarity which are desirable for many synthetic resin applications.

Furthermore, because of reactions between the organic pigments and the catalysts, antioxidants, preservatives, fungicides, vulcanizates, and other additives employed in processing the resins (which reactions become increasingly important as the processing conditions are made more severe), the number of inorganic pigments suitable for use in colouring the said resins has grown even smaller.

This invention provides coloured synthetic resins which do not undergo shade alteration upon exposure to high temperatures, for example, up to 700°F. The resins are coloured yellow shades that not only do not undergo shade alteration during forming operations at such high temperatures but also are fast to light.

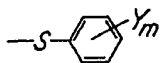
According to the present invention, a synthetic resin is coloured with an α -phenylthioanthraquinone having the structural formula:



I

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wherein each X represents hydrogen, alkyl-amino, anthraquinonylamino, or a phenylthio radical of the formula:



II

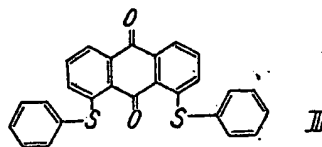
- 5 Y represents hydrogen, halogen, alkyl or alkoxy, Z represents hydrogen, halogen, alkyl or alkoxy, and is in a *beta*- position of the anthraquinone nucleus, m represents 0, 1, 2 or 3 and n represents 0, 1, 2, 3, or 4.

- 10 The *alpha*-phenylthioanthraquinones are unexpectedly superior colorants for synthetic resins, more particularly the thermoplastic resins which are obtained by polymerisation of an unsaturated organic monomer, and especially those which in the uncoloured form are
- 15 clear, substantially water-white, glass-like solids, e.g. polystyrene and polymethylmethacrylate. They are surprisingly stable and do not change colour, in admixture with such resins and the monomers from which the polymers are produced, during the normal processing procedure. Moreover, the *alpha*-phenylthioanthraquinones do not exhibit any anti-catalytic effect on monomeric substances (e.g. methyl-
- 20 methacrylate) polymerised in their presence and are not themselves adversely affected by the catalysts used in such polymerisation. Synthetic resins coloured in accordance with the invention are of pleasing and desirable bright
- 25 shades which have excellent fastness and durability characteristics (including retention of gloss on weathering). The colour is surprisingly stable to processing or forming operations at high temperatures (e.g. up to 700°F.), such as moulding, spinning and extrusion, and to the
- 30 presence of additives such as peroxides.

- 35 Thus, unsubstituted 1-phenylthio-anthraquinone, 1,4-bis(phenylthio)anthraquinone, 1,5-bis(phenylthio)anthraquinone, 1,8-bis(phenylthio)anthraquinone and 1,4,5,8-tetrakis(phenylthio)anthraquinones can be used, as well as substituted *alpha*-phenylthioanthraquinones in which (a) one or more of the phenylthio radicals are themselves substituted by 1 to 3
- 40 halogen, alkyl or alkoxy substituents, and/or (b) the anthraquinones nucleus is further *alpha*-substituted by 1 to 3 substituents which are substituted phenylthio radicals of the above class (a), alkylamino radicals or anthra-
- 45 quinonylamino radicals, and/or (c) the anthraquinone nucleus is *beta*-substituted by 1 to 4 halogen, alkyl or alkoxy substituents. The halogen substituents include especially fluorine, chlorine or bromine substituents, and the alkyl
- 50 or alkoxy substituents preferably contain 1 to 12 carbon atoms each.

- 55 The compounds in which at least two of the X's and Y and Z all represent hydrogen, and particularly those in which a phenylthio radical is present in each of the benzene nuclei of the
- 60

anthraquinone molecule (i.e. 1,5- and 1,8-bis derivatives), are preferred in view of their superior light fastness. Of these 1,8-bis(phenylthio)anthraquinone, having the structural formula:



III

is especially preferred, inasmuch as it not only imparts to thermoplastic resins bright yellow colorations having excellent stability to heat and excellent fastness to light, but also possesses a surprisingly greater tinctorial power. Thus, while equal weights of 1,8-bis(phenylthio)anthraquinone and of 1,5-bis(phenylthio)anthraquinone produce similar reddish yellow

70 shades of similar stability to heat, the strength of coloration produced by the 1,8-isomer is about twice that obtained with the 1,5-isomer.

An additional advantageous property of the said class of *alpha*-phenylthioanthraquinone is their solubility in the resins, as well as in certain of the common organic solvents (for example, acetone, toluene and ethyl acetate). The use of such colorants in accordance with the present invention to colour resins which in the normal form are clear, glass-like solids, especially polystyrene and polymethylmethacrylate, makes it possible to produce clear, bright, yellow to reddish-yellow glass-like products which do not change colour during processing at high temperatures and on exposure to sunlight, and which retain their gloss and clarity in weathering.

The incorporation of the *alpha*-phenylthioanthraquinones into the preformed resins or into monomers or co-monomers thereof, can be accomplished by methods known *per se*. For example, pellets, beads or rods (the usually available commercial forms) of the resin can be surface-coated by mixing them with the comminuted pigment in a suitable mixer, and the thus coated polymer fed to a suitable forming apparatus, e.g. a moulding press, extruder or fibre spinner. Alternatively an aqueous paste or solvent solution of the *alpha*-phenylthioanthraquinone can be mixed with the polymer in comminuted form and, after drying (to remove water or solvent), the dried mixture (with additional mixing if desired, for example, in a ribbon mixer) can be fed to a moulding press or other forming apparatus. The *alpha*-phenylthioanthraquinone can also be dissolved or suspended in the monomer or co-monomer and the resulting mixture polymerised and formed, in one or separate

115 operations, as is customary.

A preferred mode of carrying out the invention involves preparing a mixture of the *alpha*-phenylthioanthraquinone, preferably in essen-

5 tially pure and finely divided condition, and the synthetic resin in particulate form (such as granular polystyrene or polymethylmethacrylate). The mixture is tumbled in known
10 manner to surface coat the resin with the pigment, and is then fed to a suitable moulding, extrusion or spinning apparatus, or combination of such forming devices, operating at a suitable temperature between about 400°
15 and about 700°F. Examples of suitable mixtures of resin and phenylthioanthraquinone are polystyrene and 1,8-bis(phenylthioanthraquinone, and polymethylmethacrylate and 1,8-bis(phenylthioanthraquinone, in the former
20 case the forming operation is performed at a temperature between 400° and 600°F, and in the latter between 300 and 400°F. The formed coloured plastic products thus obtained are clear, bright yellow to reddish-yellow coloured articles which show no evidence of shade alteration.

25 In another method of procedure, the alpha-phenylthioanthraquinone is dissolved or suspended in the monomer form of the desired resin (e.g. methylmethacrylate) containing a suitable polymerisation catalyst (such as benzoyl peroxide), and the solution is heated to induce polymerisation in the usual manner. The resultant yellow coloured polymer can be
30 formed in any suitable manner (e.g. extruded, moulded or spun). The formed articles thus obtained have properties substantially identical with those formed by pigmenting the polymer.

35 The amount of alpha-phenylthioanthraquinone which can be used to colour the synthetic resin compositions can vary over a wide range. The particular amount used is dependent upon the depth of shade or coloration desired and the particular colorant employed, and the colorant may be added in amounts which range from the extremely minute to very large amounts limited only by the compatibility of the alpha-phenylthioanthraquinone and the particular resin being
40 coloured. Such amounts may vary to a considerable degree from resin to resin, as will be evident to those skilled in this art. Thus, light tints, for finished pieces, can be obtained with an amount of alpha-phenylthioanthraquinone as low as 0.0001 part per 100 parts by weight of the resin or resin composition. Deep shades, or master batches, are obtainable with amounts
45 up to 5.0 or more parts per 100 parts by weight of resin composition. Masterbatches can be prepared, for instance, by admixture of the alpha-phenylthioanthraquinone with the resin monomer or polymer in amounts of 0.5 to 5.0 parts, preferably from 1.0 to 3.0 parts, per 100 parts of resin composition. Products of
50 any desired lighter yellow shade can then be obtained by mixing the coloured master batch, after the usual processing and comminution, with unpigmented resin and further processing the mixture, e.g. by moulding, extruding or
55 spinning.

The alpha-phenylthioanthraquinones can be prepared in various ways. Thus, 1-phenylthioanthraquinone, 1,4- and 1,5-bis(phenylthio)anthraquinone and their alkyl and alkoxy substituted derivatives, can be produced in the
60 manner described in German Patent No. 116,951; Annales de Chimie [12] 10, page 716; and United States Patent Nos. 1,062,990; 2,109,464 and 3,018,154. For example, a suitable anthraquinone compound having a replaceable substituent in the alpha- position into which the phenylthio radical is to be introduced can be condensed with a suitable
65 thiophenol. The condensation can be effected, for example, by heating in an alcoholic reaction medium (such as methanol, ethanol, isopropanol, isobutanol, n-butanol, diethylene glycol monoethyl ether, ethylene glycol monoethyl or mixtures thereof) which also contains base
70 (such as, sodium hydroxide, potassium hydroxide, sodium carbonate, pyridine, N,N-diethylaniline or mixtures thereof), and the resulting alpha-phenylthioanthraquinone can be recovered, for example by filtering off the
75 alpha-phenylthioanthraquinone which separates out of the reaction medium as it is formed. Thus, the alpha-phenylthioanthraquinones can be prepared by mixing an alpha-chloro (or bromo or nitro) anthraquinone or one containing further alpha and/or beta substituents
80 (such as an alkylamino anthraquinone or a 4,4'-halo-1,1'-dianthrimide) with a sufficient amount of a lower alcohol to give a uniform slurry, adding a solution of thiophenol (or
85 o-, m- or p-thiocresol, or a thioxyleneol or a halogenated or alkoxy derivative of thiophenol, thiocresol or thioxyleneol) in a lower alcohol which also contains potassium hydroxide (or sodium hydroxide or sodium carbonate or potassium carbonate); heating
90 the mixture to boiling, and boiling and refluxing until the reaction is complete; filtering the resulting slurry; washing the filter-cake alkali-free with warm water, and drying. Alternatively, they can be prepared by removing
95 the sulphur groups from the corresponding alpha-phenylthioanthraquinone sulphonic acid dyestuffs (e.g. by heating with sulphuric acid); or by halogenating alpha-phenylthioanthraquinones (e.g. by brominating a phenylthioanthraquinone in solution in nitrobenzene or other solvent).

100 The alpha-phenylthioanthraquinones are preferably used in a finely divided form, which can be obtained readily in a known manner, e.g. by micropulverizing or sand grinding.

105 The following Examples illustrate the invention. Parts and percentages are by weight and temperatures are in degrees Fahrenheit.

EXAMPLE 1

125 A number of mixtures, each consisting of 100 parts of polystyrene pellets and 0.05 part of 1,8-bis(phenylthio)anthraquinone, were subjected to the following treatment.

Each mixture was placed in a metal container which was closed, and then tumbled mechanically for 5 minutes to surface coat the resin with pigment. Thereafter the coated resin was fed to a laboratory extruder operating at variable temperatures ranging from 320° to 600°, as set out in the Table below. The mass was held in the extruder for 5 minutes and then extruded at slow speed in the form of a continuous rod $\frac{1}{8}$ inch in diameter. The rods thus obtained were coloured a clear, bright reddish-yellow and showed no evidence of colour (shade) alteration. The rods were pelletized and the various masses of coloured pellets were fed to an injection moulding apparatus operating at about 400°. The pellets were thus formed into plaques approximately

2" x 3" x $\frac{1}{8}$ ", which were exposed for 320 hours in the Fade-Ometer ("Fade-Ometer" is a Registered Trade Mark) and compared with unexposed portions. No noticeable alteration in colour had occurred.

For purposes of comparison, coloured polystyrene rods were prepared in the same manner, but employing 0.05 part of the commercially available resin colorant Colour Index Solvent Yellow 40 instead of the 1,8-bis(phenylthio)anthraquinone. The colour of the resulting rods was only about half as intense as that of the rods obtained with the same amount of 1,8-bis(phenylthio)anthraquinone. In addition, the rods showed alteration in colour, as set out in the Table.

TABLE

Extrusion Temp.	1,8-Bis(phenylthio)-anthraquinone	Alteration in Colour* Colour Index Solvent Yellow 40
320°	Nil	Nil
400°	"	"
500°	"	Much
550°	"	Very much
600°	"	Very much

* Alteration rated on the following scale; nil, slight, appreciable, considerable, much, very much.

EXAMPLE 2

The procedure of Example 1 was repeated using, instead of polystyrene, a similar amount of polymethylmethacrylate ["Plexiglass" ("Plexiglass" is a Registered Trade Mark)]. The surface coated polymer was extruded at about 350° and moulded at about 325°. The pigmented polymer showed no alteration in shade upon extrusion, notwithstanding the relatively high temperature used (350°). The moulded plaque showed no noticeable change in colour after exposure in the Fade-Ometer for 320 hours.

EXAMPLE 3

A mixture of 100 parts of methylmethacrylate, 0.1 part of benzoylperoxide and 0.1 part of 1,8-bis(phenylthio)anthraquinone was heated on a steam bath until vigorous boiling occurred. The mixture was removed from the steam bath, and after the vigorous reaction subsided, it was placed in a warm (140°) oven for about 16 hours. Thereafter the polymerisation reaction was completed by heating the mass for about 1 hour on the steam bath.

The pigmented polymer was then extruded into rods as described in the above Example 2. The resulting clear, glass-like rods were coloured a bright reddish-yellow. The presence of the 1,8-bis(phenylthio)anthraquinone in the monomeric composition did not interfere with the polymerisation to any noticeable extent, nor did the presence of the peroxide catalyst cause any alteration in the colour of the pigmented polymer.

EXAMPLE 4

A mixture of 100 parts of polystyrene pellets and 0.05 part of 1-phenylthio-anthraquinone was subjected to the procedure described in above Example 1, employing an extrusion temperature of 600° and a moulding temperature of about 400°. Clear, bright yellow-coloured polystyrene was obtained, the colour of which was a somewhat greener yellow but of lesser intensity than that obtained under like conditions in Example 1. No alteration in the colour was noticeable, notwithstanding the high temperatures employed.

EXAMPLE 5

By substituting an equal amount of 1,5-bis-(phenylthio)-anthraquinone for the 1-phenylthio-anthraquinone employed in Example 4, clear, bright reddish-yellow coloured polystyrene was obtained, the colour of which was similar in shade to that obtained under like conditions in Example 1, but the colour intensity of which was considerably less. No alteration in the colour was noticeable, notwithstanding the high temperatures employed.

EXAMPLE 6

A mixture of 100 parts of polystyrene pellets and 0.05 part of 4-methylamino-1-phenylthio-anthraquinone was subjected to the procedure described in above Example 1, employing an extrusion temperature of 550° and a moulding temperature of about 400°. Clear, bright violet-coloured polystyrene was obtained. No alteration in the colour was noticeable, notwithstanding the high temperatures employed.

Minor modifications can be made in the details of these Examples and identical results obtained. Thus, various temperatures can be employed. For instance, temperatures ranging from 300° to 600°F. can be used with polystyrene; and temperatures ranging from 300° to about 400°F. can be used with polymethylmethacrylate. Moreover, in producing coloured polymers by polymerisation of the monomers, temperatures between about 120° and about 300°F. can be employed with styrene monomer and temperatures between about 100° and about 250°F. can be employed with methylmethacrylate.

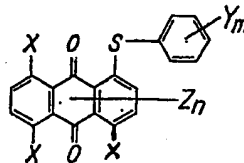
Instead of the *alpha*-phenylthioanthraquinones used in the Examples, similar amounts of the following *alpha*-phenylthioanthraquinones may be substituted: 1,4-bis-(phenylthio)anthraquinone; 1-(*o*- or *m*- or *p*-methyl-phenylthio)anthraquinone; 1-(*o*- or *m*- or *p*-chloro-phenylthio)anthraquinone; 1-(*o*- or *m*- or *p*-methoxy-phenylthio)-anthraquinone; 1-(*o*- or *m*- or *p*-ethoxy-phenylthio)-anthraquinone; 1-(4'-butyl-phenylthio)anthraquinone; 1-(4'-nonyl-phenylthio)anthraquinone; 1-(4'-dodecyl-phenylthio)anthraquinone; 1-(dimethyl-phenylthio)anthraquinone; 1-(6'-isopropyl-3'-methyl-phenylthio)anthraquinone; the corresponding 1,4-1,5- and 1,8-bis(substituted phenylthio)-anthraquinones; the corresponding 1,4,5,8-tetrakis(substituted phenylthio)anthraquinones; 4,4'-bis(phenylthio)-1,1'-dianthrimide; and brominated 1,4-bis or 1,5-bis or 1,8-bis-(phenylthio)anthraquinones.

Synthetic resins and monomers and comonomers other than those employed in the Examples can be substituted, e.g. polyethylene, polypropylene, polybutylene, fluorine-containing polymers, polyvinyl chloride, polyvinyl copolymers, polyacrylonitrile, acrylonitrile copolymers, polyamides such as the nylons, silicones and cellulose esters and ethers.

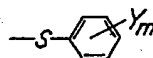
The coloured resin products can be produced in the form of articles of various shapes and sizes, including moulded pieces, sheets, films, fibres and filaments.

WHAT WE CLAIM IS:—

1. A synthetic resin coloured with an *alpha*-phenylthioanthraquinone having the structural formula:



wherein each X represents hydrogen, alkyl-amino, anthraquinonylamino or a phenylthio radical of the formula:



Y represents hydrogen, halogen, alkyl or alkoxy, Z represents hydrogen, halogen, alkyl or alkoxy, and is in a *beta*-position of the anthraquinone nucleus, m represents 0, 1, 2 or 3, and n represents 0, 1, 2, 3, or 4.

2. A coloured synthetic resin according to claim 1 in which the resin in its uncoloured form is a clear, substantially water-white, glass-like, synthetic thermoplastic solid.

3. A coloured synthetic resin according to claim 2 in which the resin is polystyrene or polymethylmethacrylate.

4. A coloured synthetic resin according to any of claims 1 to 3 containing 0.0001 to 5 parts of the said *alpha*-phenylthioanthraquinone, per 100 parts by weight of the said resin.

5. A coloured synthetic resin according to any of claims 1 to 4 coloured with 1-phenylthioanthraquinone or 1,8-bis(phenylthio)-anthraquinone.

6. A synthetic resin coloured with an *alpha*-phenylthioanthraquinone substantially as described in any one of the foregoing Examples.

7. Process for producing a coloured synthetic resin which comprises incorporating an *alpha*-phenylthioanthraquinone having the formula specified in claim 1 in a synthetic resin.

8. Process according to claim 7 in which the *alpha*-phenylthioanthraquinone is mixed with the synthetic resin and the mixture is subjected to a forming operation at a temperature between 300° and 700°F.

9. Process according to claim 8 in which the synthetic resin is polystyrene, the phenyl-

- thioanthraquinone is 1,8-bis(phenylthio)anthraquinone, and the temperature is between 400° and 600°F.
- 5 10. Process according to claim 8 in which the synthetic resin is polymethylmethacrylate, the phenylthioanthraquinone is 1,8-bis(phenylthio)anthraquinone, and the temperature is between 300° and 400°F.
- 10 11. Process according to claim 7 in which the synthetic resin in its uncoloured form is a clear, substantially water-white glass-like solid which can be obtained by polymerising the corresponding monomer, in which the *alpha*-phenylthioanthraquinone is mixed with
- 15 12. Process according to claim 11 in which the monomer is styrene and the polymerisation is carried out by heating the mixture to a temperature between 120° and 300°F. 20
13. Process according to claim 11 in which the monomer is methylmethacrylate and the polymerisation is carried out by heating the mixture to a temperature between 100° and 250°F. 25
14. Process according to claim 7 substantially as described.
15. Coloured synthetic resins produced by the process of any of claims 7 to 14. 30
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